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GAS SENSOR ARRAY BASED ON TIN OXIDE NANO STRUCTURE FOR VOLATILE ORGANIC COMPOUNDS DETECTION[#]

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Abstract. The detection of volatile organic compounds (VOCs) is essential in practical application in breath analysis. Thus, gas sensors based on metal oxide have been fabricated, but they lacked selectivity. One approach to resolve this task is to use an array of highly sensitive and selective sensors as an electronic nose. Here a gas sensor array based on Tin oxide nano-structure with temperature modulation techniques was presented. A Platinum micro-heater is accompanied with the array gas sensor. The gas sensor array was composed of five single sensors, and that single sensor is located at different site from the micro heater and works at different temperatures. The gas sensing properties of the gas array sensors were investigated with VOC gases such as Ethanol, Methanol, Iso-propanol, and Acetone as well as NH_3, H_2, and H_2S. We also confirm the good selectivity of the array sensor for Ethanol, Methanol, Iso-propanol, Acetone, NH_3, H_2, and H_2S by using radar graphic method.

Keywords: gas sensor, gradient sensor array, electronic nose, Tin oxide nanowire.

Classification numbers: 2.2.2, 2.4.2, 2.10.2.

1. INTRODUCTION

Volatile Organic Compounds (VOCs) consist of varieties of organic compounds that are vapor at room temperature. In general, VOCs are released from burning fuel such as gasoline,

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wood, coal, or natural gas [1]. VOCs are harmful when they are absorbed into the human body, thus can cause respiratory, allergic, or immune effects in infants or children [2, 3]. Also, gas sensors are becoming transversally crucial in many fields, such as food and beverage quality, agriculture, security against terrorism, and medical diagnosis[4–7]. Metal oxides (MOs) can be used as gas sensors in many applications thanks to their high sensitivity to a wide range of gases and compounds. As a simple principle of gas sensor-based MOs, resistant of MOs sensing layer would be changed when a VOC is adsorbed and thus has attracted significant attention as the VOC-sensing layer. Furthermore, resistive sensors are simple and cheap and can be used to realize a network of integrated devices, which is crucial nowadays [5, 8, 9]. MOs sensing layer based single VOCs gas sensor possesses many advantages such as easy processing, low cost, but it also suffers from low selectivity, sensitive to one chemical contaminant, and cannot produce all the information for many chemical species [4]. To deal with the dis-advantage of a single VOC sensor, an array gas sensor in so-called electronic noses is necessary to detect the several contaminants in single device. There are several structure designs of the array gas sensor, such as P. Breuil *et al.* [10] developed three identical gas sensor arrays by combining single commercial semiconductor gas sensors. H. Moon *et al.* made an array gas sensor based on metal oxide thin film, metal-catalyzed ones, and nano-structure ones to enhance sensitive detection of H_2S, NH_3, and NO [11]. Tin-oxide nanospheres and copper oxide nanoflower-decorated grapheme based array gas sensor was developed by D. Zhang *et al.* [12] to detect a mixture of ammonia and formaldehyde at room temperature.

In this work, an array gas sensor composing of five single gas sensors is developed. Platinum micro-heater is integrated into the array sensor to activate the working temperature of the array sensor. The temperature of each single sensor in the array was evaluated by infrared emission images. Gas sensing properties of the array sensor was measured for seven gases (Ethanol, methanol, Iso-propanol, Acetone, NH_3, H_2, and H_2S). In order to demonstrate the ability of the array gas sensor to discriminate different gases species through multi-channel pattern recognition [13-15], gas sensor responses of each the single sensor in the array at the power of 165 mW are plotted in a radar plot.

2. EXPERIMENTAL

The array gas sensor was realized using an on-chip approach, as in Figure 1. First, the Tin oxide (SnO_2) nanowires were grown directly on the electrode by a CVD method as follows [16]: using photolithography and DC sputtering techniques, a patterned of SiO_2, Pt, Au, and SiO_2 were deposited with the shape of 5 sensors and Pt micro-heater. The sample was then placed inside a horizontal quartz tube furnace on top of a ceramic vessel containing Sn powder (Merck, 99.9 %). The temperature was risen to 750 ^oC from room temperature and kept for 12 minutes while O_2 gas was passed through the tube at flow rates of 0.5 sccm. The furnace was then switched off and cooled to room temperature. Second, to measure signals of the array sensor, the electrode with SnO_2 nanowires on it would be contacted to a pad for multi-sensor by gel of Ag. The pad was then treated at 90 ^oC for 15 minutes to make good contact between pins on electrode and pins on the pad. The pins on the pad would connect to the data acquisition system by wirings, which were soldered at these pins of the pad. Finally, signals for the gas sensor array were measured by a customization data acquisition system. We have used the Arduino mega 2560 module as a main component of the system. This kind of module is widely used open-source single-board microcontroller development for a platform with flexible, easy-to-use hardware and software components [17]. Signals of the array sensor were measured on reference resistances

connected in series with a single sensor in the array sensor. The entire connection of the Arduino module to the array sensor is conducted by a hand-made customized program based on Labview programming. The array sensor was measured at different gases (Ethanol, Acetone, NH_3, H_2, and H_2S) diluted in the air at different concentrations. The synthetic materials are characterized by X-ray diffraction (XRD) and emission field scanning electron microscope (FE-SEM), respectively. Gradient temperature, as well as temperature's single sensor was characterized by Infrared Emission Images method.

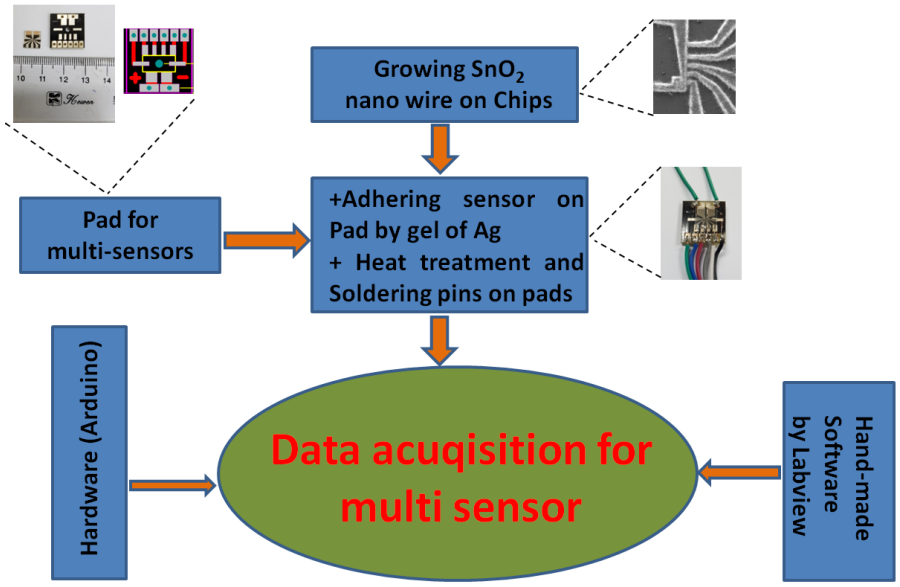

Figure 1. Flow chart for SnO_2 nanowires-based array gas sensor.

3. RESULTS AND DISCUSSION

3.1. SEM images of the array gas sensor

The morphology and microstructure of the array gas sensor were illuminated by SEM observations. A panoramic low-magnification SEM image of the array sensor on a large scale is shown in Fig. 2A. As shown in Figure 2A, the array sensor contains one Pt micro-heater with

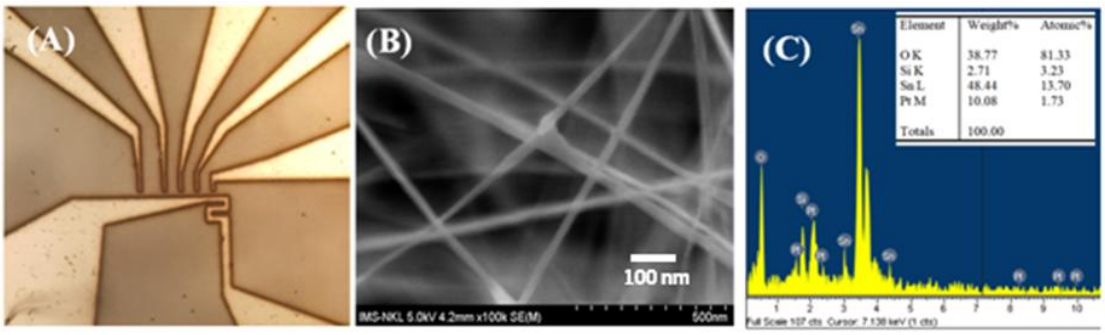

Figure 2. (A) Low and (B) high magnification SEM images of the array sensor; (C) EDX showing the elements present in the decorated SnO_2 nanowires.

constant width at center and SnO_2 nanowires were grown around each five sensors on the array sensor. Figure 2B shows the high-magnification SEM images of the array gas sensor. As can be seen that SnO_2 nanowires are smooth, straight and a homogeneous. The analysis of several SEM images showed that the average diameter of SnO_2 nanowires is 30±10 nm. The EDX spectrum in Figure 2C demonstrates that SnO_2 nanowires in Figure 2B only contain tin, oxide, and platinum of heater. As can be seen in the legend, the atomic percentage of tin and oxygen agree with the stoichiometry of SnO_2 nanowires.

3.2. Gradient temperature of the array sensor

To evaluate gradient temperature of the array sensor, gradient simulation results on COMSOL Multiphysics Software and real gradient temperature on-chip by Infrared Emission Images were collected. Figure 3A is a simulation result on COMSOL. According to Figure 3A, the highest temperature was at the center of temperature, which is the area with the smallest width of Pt heater. Gradient temperature was in the shape of a shell and had perfect symmetry through the center. The temperature of each sensor from the center is about 380 ^oC; 350 ^oC; 290 ^oC; 240 ^oC; and 190 ^oC, respectively. Because the area of sensing layer is quite small, only about

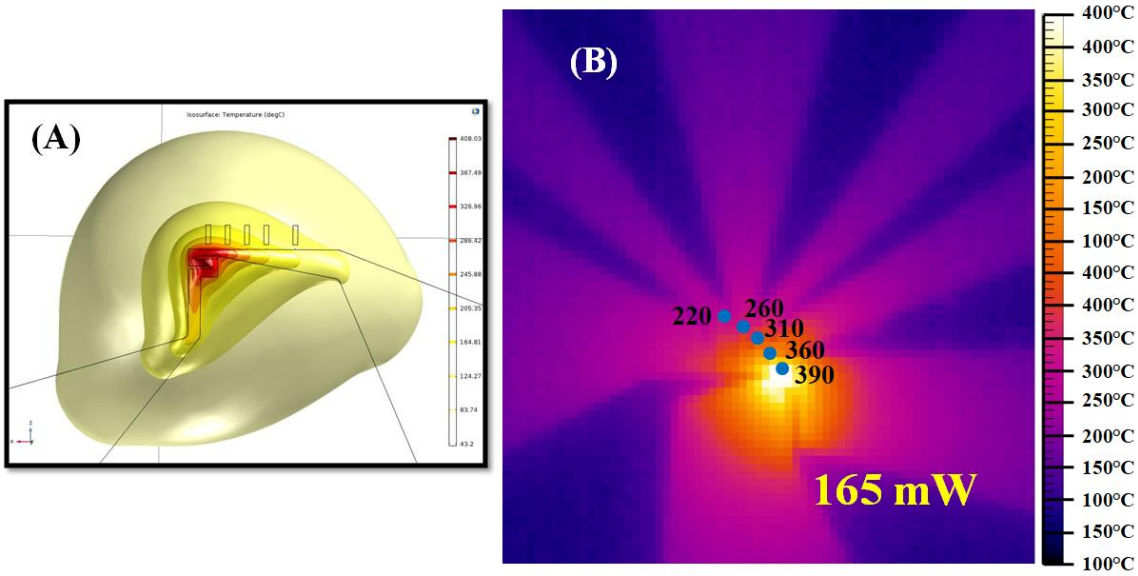

Figure 3. Gradient temperature (A) simulation on COMSOL, and (B) Infrared Emission Image on chip.

300 × 300 μm^2, the temperature of each sensor in the array sensor can't be determined directly. Therefore, Infrared Emission Images to evaluate the real gradient temperature of the array sensor were used in this work. Figure 3B is an Infrared Emission Image at a power of 165 mW of heater. The sensor in the center of temperature has the highest temperature, and the others have lower temperatures due to longer distance from the center. The temperature distribution of each sensor in the array sensor is 390 ^oC; 360 ^oC; 310 ^oC; 260 ^oC; and 220 ^oC, respectively. The results were relatively the same as the mentioned simulation ones.

3.3. Gases sensing characteristics the array gas sensor

The array gas sensor is measured at the power of 165 mW and for seven gases (Ethanol, Methanol, Iso-propanol, Acetone, Hydrogen-H_2, Ammonia-NH_3, Hydrogen Sulfide-H_2S) diluted in the air at different concentrations as in Table 1. Since seven gases are reducing gases, the responses of the array gas sensor along this paper is defined as $\boldsymbol{S = V_a/V_g}$, where $\boldsymbol{V_a}$ is the voltage of each sensor in the array gas sensor in air and $\boldsymbol{V_g}$ is voltages of each sensor in presence

Table 1. Concetrations tested for each gas, in Part Per Million.

Gas	**Concentrations** (Part Per Million – **ppm**)			
Ethanol	15.0	125.0	625.0	2500.0
Methanol	60.0	310.0	1560.0	6250.0
Iso-propanol	20.0	100.0	500.0	2000.0
Acetone	50.0	250.0	1000.0	5000.0
Hydrogen	6.0	25.0	100.0	400.0
Ammonia	6.0	25.0	100.0	400.0
Hydrogen Sulfide	0.25	1.0	4.0	10.0

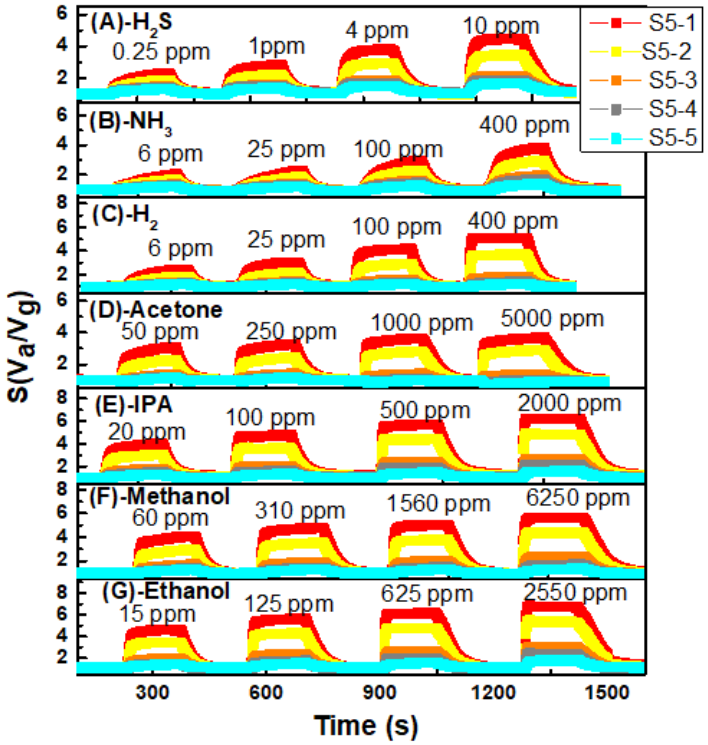

Figure 4. Gas sensitivity at power of 165 mW when exposed to (A) **H_2S**, (B) **NH_3**, (C) **H_2**, (D) **Acetone**, (E) **IPA**, (F) **Methanol**, (G)-**Ethanol** with different concentrations.

of the target gases. S5-1, S5-2, S5-3, and S5-4 are the abbreviation of each sensor in the array sensor, which has a different distance from the center of temperature. S5-1 is the nearest sensor from the center of temperature, S5-2 is another sensor is farther from the center of temperature

than S5-1, and so on for S5-3, S5-4, and S5-5. Figure 4(A-G) shows the typical response curves of the array gas sensor to 7 gases with different concentrations, as mentioned above. The array sensor was all sensitive to the gases, including VOCs and non-VOCs. It is clear that each sensor in the array sensor responses increases with increasing the concentration of target gases. As shown in Figure 4(A-G), gas sensor responses of S5-1, S5-2, S5-3, S5-4, and S5-5 are ordered from high to low, respectively. Gas sensor responses to all gases of S5-1 are always the highest compared to the others. These results are attributed to the gradient temperature principle of the array gas sensor. The S5-1 sensor is the nearest one located in the center of temperature, so its working temperature is the highest compared to the others. Because of this reason, the S5-1 sensor always show the highest sensitivity and has faster response/recovery time in comparison with the S5-2, S5-3, S5-4, and S5-5 sensor. Moreover, the array gas sensor demonstrates also differences of gas sensing properties between inorganic gases (in this case, those gases are H_2S, NH_3, H_2) to VOCs (Ethanol, methanol, Iso-propanol, and Acetone). Gas sensing properties of the array sensor such as sensor response, response time, and recovery time to inorganic gases always show lower than those of VOCs. These properties result in the advantage of discrimination in gases using only gas sensing properties without the need for complicated machine learning algorithms [11, 12, 14–16].

Each curve in the plot of Figure 5 represents the gas sensor response for one gas. Based shape of the radar plots in Figure 5, it seems that it can be divided into five groups: Ethanol, Iso-propanol, Methanol is in one group because of the same shape of radar plots; Hydrogen, Ammonia, Hydrogen Sulfide, and Acetone are in 5 different groups, respectively.

The enclosed areas of the plots are extracted in Figure 6. It is clear that each gas produces a different enclosed area. Although there are some differences between the plots in Figure 5, if we combine shape of radar plots and the enclosed area of each gas as in Figure 6, each gas in seven gases can be distinguished clear by using the array gas sensor. It can be concluded that the radar plots are good fingerprints for four VOC gases (Ethanol, Methanol, Iso-propanol, Acetone) and three inorganic gases (Ammonia, Hydrogen, Hydrogen Sulfide).

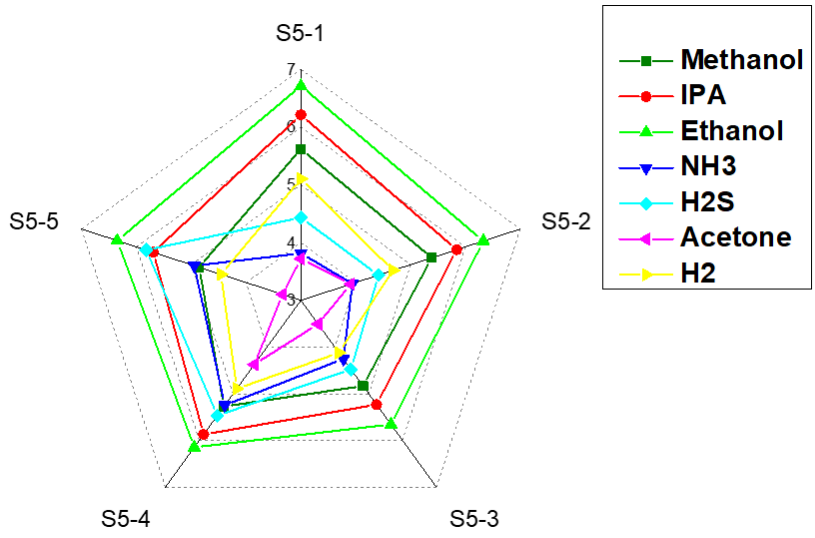

Figure 5. Radar plot of sensor responses of five sensor elements in the array gas sensor in a static system when exposed to volatiles of Methanol, IPA, Ethanol, Ammonia, Hydrogen sulfide, Acetone, and Hydrogen at power of 165 mW.

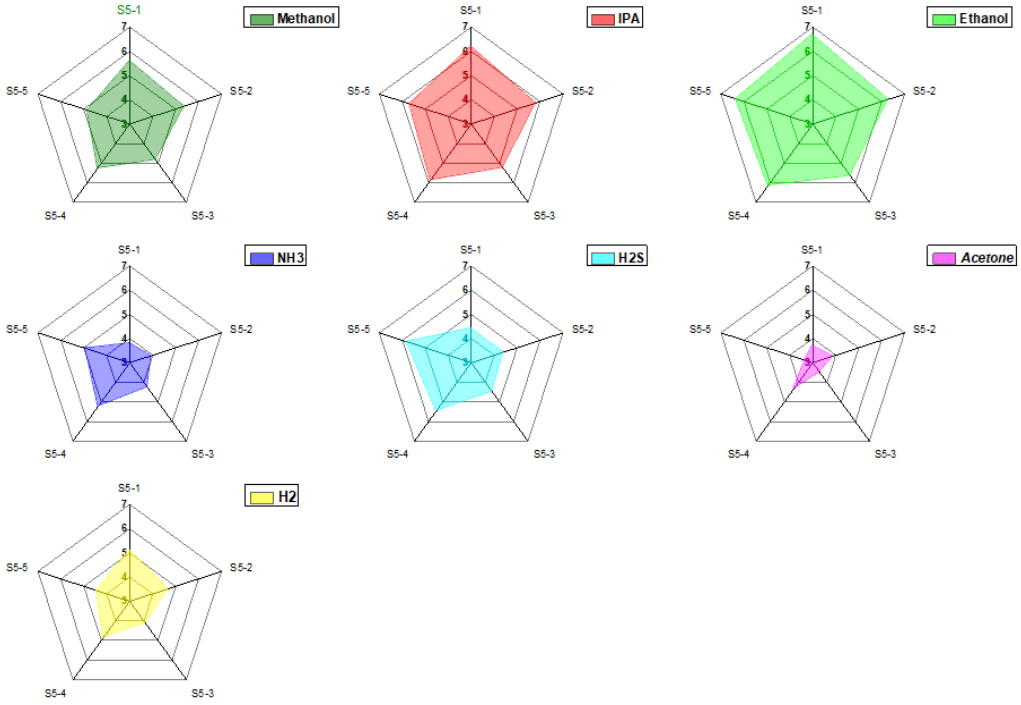

Figure 6. Enclosed area extracting from radar plot for the sensor array at power of 165 mW.

4. CONCLUSIONS

An array gas sensor was fabricated by the CVD method. The array gas sensor is operated based on the gradient temperature principle with the heat source creating by supplying voltage to the Platinum-based micro-heater. The working temperature of each sensor in the array gas sensor is different at the given voltage, which is provided to micro-heater because the distance from that sensor to the heat source is difference. The array sensor was exposed to different gases, including VOC gases, as well as inorganic gases at the power of 165 mW. The radar plots of gas sensor response to the gases show that the array gas sensor exhibits perfect discrimination for these gases.

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